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(71) Applicant: Canon Kabushiki Kaisha

(72) Inventor: Tatsuya IWASAKI

(72) Inventor: Tohru DEN

(74) Agent: Patent Attorney, Tokuhiro WATANABE

(54) [Title of the Invention] NANOSTRUCTURE AND METHOD FOR  
MAKING THE SAME

(57) [Abstract]

[Object] To provide a nanostructure including an anodized film having highly uniform nanoholes suitable for advanced function device applications.

[Solving Means] A nanostructure includes a substrate having a conductive surface; an anodized film with nanoholes on the conductive surface; oxide layers between the bottoms of the nanoholes and the conductive surface; and paths in the oxide layers. The paths connect the bottoms of the nanoholes to the conductive surface and contain the material that constitutes the conductive surface.

[Claims]

[Claim 1] A method for making a nanostructure comprising a substrate having a conductive surface, an anodized film with nanoholes on the conductive surface, oxide layers between the bottoms of the nanoholes and the conductive surface, and paths in the oxide layers, the paths connecting the bottoms of the nanoholes to the conductive surface and comprising the material that constitutes the conductive surface, the method comprising the steps of:

- 1) forming an aluminum-containing film on the conductive surface of the substrate, the conductive surface containing at least one element selected from Ti, Zr, Nb, Ta, and Mo; and
- 2) applying a voltage between the aluminum-containing film and a counter electrode to anodize the aluminum-containing film so as to form the anodized film with nanoholes, wherein, in said step 2), the anodization is performed while monitoring an anodization current and is stopped after a change in the anodization voltage indicating that the anodization has proceeded up to the conductive surface is detected.

[Claim 2] A method according to claim 1, wherein the anodization is stopped after the anodization current has dropped to 1 mA/cm<sup>2</sup> or less.

[Claim 3] A method according to claim 1, further comprising

the step of heating after said step 2).

[Claim 4] A method according to claim 3, wherein the step of heating is performed in a reducing atmosphere.

[Claim 5] A method according to claim 3 or 4, wherein the step of heating includes heating at 300°C or more.

[Claim 6] A method according to claim 1, wherein the conductive surface contain Nb or Ti.

[Claim 7] A method according to claim 1, further comprising the step of filling the nanoholes with at least one of a metal and a semiconductor after said step 2).

[Claim 8] A method according to claim 4, further comprising the step of filling the nanoholes with at least one of a metal and a semiconductor after said step of heating the nanostructure.

[Claim 9] A method according to one of claims 7 and 8, wherein the step of filling the nanoholes with at least one of the metal and the semiconductor includes a contact step of bringing the nanostructure into contact with a melt of the metal and/or the semiconductor for filling the nanoholes.

[Claim 10] A method according to claim 9, wherein the contact step is performed under a pressure.

[Claim 11] A method according to any one of claims 7 to 10, wherein the metal and the semiconductor are each at least one selected from In, Sn, Al, Se, Te, GaSb, and Bi<sub>2</sub>Te<sub>3</sub>.

[Claim 12] A method according to any one of claims 7 to 10,

wherein the metal and the semiconductor are each at least one selected from Ag, Au, Cu, and Ge.

[Claim 13] A method for making a nanostructure comprising a substrate having a conductive surface containing at least one element selected from Cu, Zn, Au, Pt, Pd, Ni, Fe, Co, and W, and an anodized film with nanoholes on the conductive surface, the nanoholes extending up to the conductive surface, the method comprising the steps of:

- 1) forming an aluminum-containing film on the conductive surface of the substrate, the conductive surface containing at least one element selected from Cu, Zn, Au, Pt, Pd, Ni, Fe, Co, and W; and
  - 2) applying a voltage between the aluminum-containing film and a counter electrode to perform anodization so as to form the anodized film with nanoholes,
- wherein, in said step 2), a current limit is imposed on the anodization voltage output.

[Claim 14] A method according to claim 13, wherein the value of the current limit is less than 50 mA/cm<sup>2</sup>.

[Claim 15] A method according to claim 13, further comprising the step of filling the nanoholes with at least one of a metal and a semiconductor after said step 2).

[Claim 16] A method according to claim 15, wherein the step of filling the nanoholes with at least one of the metal and the semiconductor includes a contact step of bringing the

nanostucture into contact with a melt of the metal and/or the semiconductor for filling the nanoholes.

[Claim 17] A method according to claim 16, wherein the contact step is performed under a pressure.

[Claim 18] A method according to any one of claims 15 to 17, wherein the metal and the semiconductor are each at least one selected from In, Sn, Al, Se, Te, GaSb, and  $\text{Bi}_2\text{Te}_3$ .

[Claim 19] A method according to any one of claims 15 to 17, wherein the metal and the semiconductor are each at least one selected from Ag, Au, Cu, and Ge.

[Claim 20] A nanostructure comprising a substrate having a conductive surface, an anodized film with nanoholes on the conductive surface, oxide layers between the bottoms of the nanoholes and the conductive surface, and paths in the oxide layers, the paths connecting the bottoms of the nanoholes to the conductive surface and comprising the material that constitutes the conductive surface.

[Claim 21] A nanostructure according to claim 20, wherein the conductive surface contains at least one element selected from Ti, Zr, Nb, Ta, and Mo.

[Claim 22] A nanostructure according to claim 21, wherein the conductive surface contains Ti or Nb.

[Claim 23] A nanostructure made by the method of claim 1.

[Claim 24] A nanostructure made by the method of claim 13.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to a nanostructure with nanoholes fabricated by aluminum anodization. The structure has a wide application range including functional devices, such as electronic devices and microdevices, and structural components. The structure may be used as an anodized film that functions as an antiwear material or an insulating material.

[0002]

[Description of the Related Arts] A thin film, a thin wire, or a dot of a metal or a semiconductor smaller than a particular size in some cases exhibits peculiar electrical, optical, and/or chemical characteristics due to restriction of electronic motion. Because of these characteristics, much attention has been drawn to a material having a structure finer than 100 nanometers, i.e., a nanostructure, for use as a functional material.

[0003] A nanostructure is made by, for example, semiconductor processing technology. Examples of thereof include fine pattern writing techniques such as photolithography, electron-beam lithography, and X-ray lithography.

[0004] In addition to these techniques, an attempt has been made at making a novel nanostructure based on a naturally occurring periodic structure, i.e., a self-organized

structure. According to this technique, a peculiar structure finer than the conventional nanostructure may be realized depending on the fine structure used as the base. Extensive investigation has been made on this technique.

[0005] An example of a self-organized peculiar structure is an anodized aluminum film (for example, refer to R. C. Furneaux, W. R. Rigby and A. P. Davidson, NATURE, Vol. 337, p. 147 (1989)). A porous oxide film is formed by anodizing an aluminum board in an acid electrolyte.

[0006] As shown in Fig. 3(c), the porous oxide film is characterized by its peculiar geometric structure comprising extremely fine cylindrical nanoholes 14 having a diameter of several to several hundred nanometers aligned in parallel rows at an interval of several to several hundred nanometers. The cylindrical nanoholes 14 have a high aspect ratio and high uniformity in diameter at cross-sections. To a certain extent, the diameter and the interval of the nanoholes 14 can be controlled by adjusting the current and voltage during anodization.

[0007] Due to the peculiar geometric structure, the anodized aluminum film has been applied to various uses, and an extensive study has been made by Masuda. Below are some examples of the application. Due to the antiwear property and the insulating property, the anodized film is applied to coating. The anodized film may be isolated and may be used

as a filter. A technique of filling nanoholes with a metal or a semiconductor or a technique of making a replica of the nanoholes may be employed to use the anodized film in coloring, magnetic recording media, electroluminescent devices, electrochromic devices, optical devices, solar cells, and gas sensors. The anodized film may also be applied to many fields including quantum-effect devices such as quantum fine wires and MIM devices, and molecular sensors using the nanoholes as chemical reaction sites (Masuda, SOLID STATE PHYSICS, 31, 493 (1996)).

[0008] The production of nanostructures using the semiconductor processing technology described above has drawbacks such as low yield and high equipment cost. A simple technology that can produce nanostructures at high reproducibility is desired.

[0009] A self-organization technique, in particular, an aluminum anodization technique, is advantageous since nanostructures can be easily formed at good controllability. Moreover, generally, large-area nanostructures can be produced by the self-organization technique.

[0010] For example, Japanese Patent Laid-Open No. 63-187415 discloses a magnetic recording medium comprising a substrate, an electrochemically stable conductive base layer on the substrate, and an anodized film of aluminum or an aluminum alloy on the base layer, wherein the anodized film has



nanoholes filled with a magnetic material. The specification discloses that the base layer should be formed by Rh, Nb, Ta, Au, Ir, Pt, Ti, Cr, Pd, Ru, Os, Ga, Zr, Ag, Sn, Cu, Hf, Be, or the like so that the depth of the nanoholes formed by anodization of aluminum or an aluminum alloy can be made uniform.

[0011] Japanese Patent Publication No. 1-237927 discloses a magnetic recording medium in which an anodized film of a metal other than aluminum and aluminum alloys is provided between a nonmagnetic substrate and an anodized film of aluminum or an aluminum alloy so as to eliminate barrier layers from the bottoms of the nanoholes in the anodized film, thereby improving efficiency of nanohole plating.

[0012]

[Problems to be Solved by the Invention] In manufacturing highly functional devices using nanoholes in anodized aluminum films, the conditions of numerous nanoholes in the anodized film, e.g., the depth of the nanoholes and the conductivity of the bottoms of the nanoholes, are preferably as uniform as possible. Conventionally, anodization has mainly been controlled by adjusting the time of anodization. The present inventors have found that conditions of nanoholes in an anodized film largely depend on the material of the base layer of the anodized film and that nanoholes with highly uniform conditions are rarely formed by merely

adjusting the time of anodization in controlling anodization.

[0013] Thus, an object of the present invention is to provide a nanostructure in which nanoholes in an anodized film have highly uniform conditions and which can be applied to advanced functional devices, and to provide a method for making the nanostructure.

[0014]

[Means for Solving the Problems] The above-described problem can be overcome by the structure and the manufacturing method of the present invention described below. An aspect of the present invention provides a method for making a nanostructure comprising a substrate having a conductive surface, an anodized film with nanoholes on the conductive surface, oxide layers between the bottoms of the nanoholes and the conductive surface, and paths in the oxide layers, the paths connecting the bottoms of the nanoholes to the conductive surface and comprising the material that constitutes the conductive surface, the method comprising the steps of 1) forming an aluminum-containing film on the conductive surface of the substrate, the conductive surface containing at least one element selected from Ti, Zr, Nb, Ta, and Mo; and 2) applying a voltage between the aluminum-containing film and a counter electrode to anodize the aluminum-containing film so as to form the anodized film with nanoholes, wherein, in step 2), the anodization is

performed while monitoring an anodization current and is stopped after a change in the anodization voltage indicating that the anodization has proceeded up to the conductive surface is detected.

[0015] According to this aspect of the present invention, the bottoms of the nanoholes in the anodized film are connected to the conductive surface via the paths composed of elements that constitute the conductive surface. As a result, a nanostructure having uniform nanoholes having the bottoms that exhibit high conductivity can be made.

[0016] Moreover, the conductivity of the bottoms of the nanoholes can be further improved by heating the nanostructure or by heating the nanostructure in a reducing atmosphere after the anodization has stopped.

[0017] Another aspect of the present invention provides a method for making a nanostructure comprising a substrate having a conductive surface containing at least one element selected from Cu, Zn, Au, Pt, Pd, Ni, Fe, Co, and W, and an anodized film with nanoholes on the conductive surface, the nanoholes extending up to the conductive surface, the method comprising the steps of 1) forming an aluminum-containing film on the conductive surface of the substrate, the conductive surface containing at least one element selected from Cu, Zn, Au, Pt, Pd, Ni, Fe, Co, and W; and 2) applying a voltage between the aluminum-containing film and a counter

electrode to anodize the aluminum-containing film so as to form the anodized film with nanoholes, wherein, in step 2), a current limit is imposed on the anodization voltage output.

[0018] According to this aspect of the present invention, a nanostructure having nanoholes extending up to the conductive surface can be reliably formed.

[0019] Another aspect of the present invention provides a nanostructure comprising a substrate having a conductive surface, an anodized film with nanoholes on the conductive surface, oxide layers between the bottoms of the nanoholes and the conductive surface, and paths in the oxide layers, the paths connecting the bottoms of the nanoholes to the conductive surface and comprising the material that constitutes the conductive surface. According to this aspect, a nanostructure including nanohole bottoms that exhibit uniform conductivities can be made.

[0020] Another aspect of the present invention provides a nanostructure made by a method comprising the steps of 1) forming an aluminum-containing film on the conductive surface of the substrate, the conductive surface containing at least one element selected from Ti, Zr, Nb, Ta, and Mo; and 2) applying a voltage between the aluminum-containing film and a counter electrode to anodize the aluminum-containing film so as to form the anodized film with nanoholes, wherein, in step 2), the anodization is performed

while monitoring an anodization current and is stopped after a change in the anodization voltage indicating that the anodization has proceeded up to the conductive surface is detected.

[0021] Another aspect of the present invention provides a nanostructure made by a method comprising the steps of 1) forming an aluminum-containing film on the conductive surface of the substrate, the conductive surface containing at least one element selected from Cu, Zn, Au, Pt, Pd, Ni, Fe, Co, and W; and 2) applying a voltage between the aluminum-containing film and a counter electrode to anodize the aluminum-containing film so as to form the anodized film with nanoholes, wherein, in said step 2), a current limit is imposed on the anodization voltage output.

[0022] According to these aspects of the present invention, a nanostructure with nanoholes in highly uniform conditions that can be applied to highly functional devices can be formed. In the present invention, an anodized aluminum film can be formed on any desired substrate by selecting the material of the conductive layer.

[0023] According to the present invention, the anodized aluminum film can be applied to various uses including quantum fine wires, MIM devices, molecular sensors, coloring, magnetic recording media, electroluminescent devices, electrochromic devices, optical devices, solar cells, gas

sensors, antiwear insulation-resistant films, filters, and the like. The present invention significantly expands the application range of the anodized films.

[0024] According to the methods of the present invention, a nanostructure including a conductive layer and an anodized aluminum film on the conductive layer can be formed.

Moreover, the nanostructure of the present invention has superior heat resistance, and a good electrical connection can be formed between a nanohole filler and the conductive layer.

[0025]

[Embodiments] Preferred embodiments of the present invention will now be described. Fig. 1 is a schematic illustration of a nanostructure of the present invention. Fig. 1(a) is a plan view and Fig. 1(b) is a cross-sectional view taken along line AA.

[0026] In Fig. 1, reference numeral 10 denotes a substrate, 11 denotes a conductive layer, 13 denotes an anodized aluminum film, and 14 denotes nanoholes. The nanoholes may be filled with a desired metal or semiconductor material by an electrochemical process.

[0027] The substrate 10 may be composed of a desired material. Examples of the material include insulating materials such as quartz glass, semiconductor materials such as Si, and various metal materials.

[0028] The material of the conductive layer 11 may be selected according to the intended use. As described in EXAMPLES below, the conductive layer may contain Ti, Zr, Nb, Ta, Mo, Cu, Zn, Au, Pt, Pd, Ni, Fe, Co, W or the like as the primary component.

[0029] The conductive layer may be selected to produce a nanostructure having superior heat resistance. In a conventional structure shown in Fig. 3(a) comprising an anodized aluminum film or in a conventional structure shown in Fig. 3(b) comprising a partially anodized aluminum film, the heat resistance limit is the melting point of aluminum. Even at a temperature below the melting point, the anodized aluminum film sometimes crack at a temperature of 300°C or more. The heat resistance can be enhanced by providing the anodized aluminum film on the conductive layer, as in the present invention. For example, the conductive layer is preferably composed of Nb. A nanohole structure with a Nb undercoat can withstand heat treatment of at least up to 1,100°C. Thus, high-temperature processing is possible, and the range of choice of the material for filling the nanoholes can be widened. Moreover, the chemical stability of the nanoholes can be enhanced by heating.

[0030] When Ti, Zr, Nb, Ta, Mo, or the like is used in the conductive layer for undercoating, oxide of the material of the conductive layer is sometimes formed at the bottoms of

the nanoholes. In such a case, the nanoholes may be heat-treated in a reducing atmosphere such as hydrogen to reduce the oxide and improve the conductivity of the bottoms of the nanoholes.

[0031] In the present invention, when the substrate contains any one of Ti, Zr, Nb, Ta, Mo, Cu, Zn, Au, Pt, Pd, Ni, Fe, Co, and W as the primary component, the conductive layer is not necessary. In the present invention, the conductive layer may have a multilayer structure such as a Ti/Ni structure.

[0032] In the present invention, the thickness of the conductive layer is designed taking into account the following items in addition to the intended use. When the substrate has conducting properties, the thickness of the conductive layer on the substrate should only be large enough to cover the substrate, and the thickness is set in the range of 10 nm to 100  $\mu\text{m}$ .

[0033] When the substrate has insufficient conducting properties, the conductive layer functions as an electrode during the step of anodization. In other words, during anodizing of a layer containing aluminum as the primary component over the entire thickness, the layer containing aluminum as the primary component becomes oxidized as the anodization proceeds, thereby increasing the resistance of the layer. As a result, a voltage drop sometimes occur due



to contribution of the resistance of the conductive layer. From this point of view, the conductive layer preferably has sufficient conducting properties, i.e., the conductive layer is preferably flat and has a thickness that can ensure satisfactory layer quality. Since the preferable thickness range is determined by the conductivity  $\rho$  of the material of the conductive layer, the area of the conductive layer, and the like, the exact range cannot be exactly defined. In general, the thickness is approximately in the range of 10 nm to 100  $\mu\text{m}$ , and preferably in the range of 50 nm to 1  $\mu\text{m}$ .

[0034] The anodized aluminum film 13 is formed by anodizing a layer containing aluminum as the primary component. The anodized aluminum film 13 contains aluminum and oxygen as the primary components and has numerous cylindrical nanoholes, as shown in Fig. 1.

[0035] The cylindrical nanoholes 14 in the anodized aluminum film 13 extend in a direction substantially perpendicular to the film surface. The nanoholes are aligned in parallel rows at a substantially regular interval. Moreover, as shown in Fig. 1a), the nanoholes tend to align into a triangle grid.

[0036] The diameter  $2r$  of each nanohole is several nanometers to several hundred nanometers. The interval  $2R$  of the nanoholes is several nanometers to several hundred nanometers, and the depth of the nanoholes is in the range

of 10 nm to 100  $\mu\text{m}$ .

[0037] To some extent, the interval and the diameter of the nanoholes can be controlled by adjusting the concentration and the temperature of the electrolyte used in the anodization, the direction of anodization voltage application, the voltage value, the time, and the conditions of the subsequent pore-widening process.

[0038] In the structure of the present invention, the layer containing aluminum as the primary component is oxidized over the entire film thickness, i.e., from the film surface up to the conductive layer. In other words, the bottoms of the nanoholes are at the conductive layer. Hereinafter, this structure is referred to as the "on-conductive-layer nanoholes". For example, when the conductive layer is composed of Ti, the structure is called "on-Ti nanoholes".

[0039] As shown in Fig. 6a), when the conductive layer as an undercoat is composed of Ti, Zr, Nb, Ta, Mo, or the like, an oxide layer 17 containing the material constituting the conductive layer, aluminum, and oxygen is formed at the bottom of each nanohole. The oxide layer 17 has a path 16 that connects the nanohole bottom to the conductive layer, the path 16 containing a large amount of elements constituting the conductive layer 11. Presumably, when anodization is continued after the barrier layer at the bottom of the nanohole has reached the underlying conductive

layer, the substances that constitute the conductive layer diffuse into the nanohole bottom, thereby producing the path. Compared to a conventional anodized alumina having a barrier layer at the nanohole bottoms, the nanoholes with the paths can be plated with a metal or a semiconductor by electrodeposition at a lower voltage with a good controllability during the subsequent electrodeposition step. Moreover, since the path is conductive, a good electrical connection can be formed between the filler in the nanohole and the conductive layer.

[0040] The nanostructure including the paths may be heated in a hydrogen gas or an inert gas atmosphere to further improve the conducting properties of the paths. As a result, uniform deposition, i.e., deposition with a small variation in the deposited amount among the nanoholes can be achieved during the electrodeposition. The conducting properties are improved presumably due to reduction of the path.

[0041] On the other hand, as shown in Fig. 6b), when the conductive layer as an undercoat is composed of Cu, Zn, Au, Pt, Pd, Ni, Fe, Co, W, or the like, no aluminum oxide, i.e., the barrier layer, exists at the nanohole bottoms. The nanoholes are formed as through holes.

[0042] It should be noted that a novel nanostructure can be produced by filling the anodized nanoholes of the nanostructure of the present invention with a metal, a

semiconductor, or the like, or by making a replica of the nanoholes.

[0043] A method for making the nanostructure of the present invention will now be described in detail with reference to Fig. 2. The description below is in the order of Fig. 2a) to Fig. 2b), and the following steps a) to e) correspond to a) to e) of Fig. 2.

[0044] a) Forming the conductive layer 11 on the substrate 10

The conductive layer 11 may be formed by a desired layer-forming method such as resistance heating deposition, EB deposition, sputtering, CVD, or plating.

[0045] b) A layer 12 containing aluminum as the primary component is formed on the conductive layer 11 so as to prepare a sample 41. The layer containing aluminum as the main component may be made by a desired film-forming method such as resistance heating deposition, EB deposition, sputtering, CVD, or plating.

[0046] c) Anodization process

The sample 41 is anodized to make the nanostructure of the present invention. To be more specific, the anodization process of the present invention includes placing the material having a layer containing aluminum as the primary component in an electrolyte and applying an anodization voltage between the material and the cathode. In this

process, the layer containing aluminum as the primary component is oxidized over the entire thickness, i.e., until the bottoms of the nanoholes reach the conductive layer.

The anodizing apparatus used in this process is schematically shown in Fig. 4.

[0047] Referring to Fig. 4, reference numeral 40 denotes a thermostat, 41 denotes the sample, 43 denotes an electrolyte, 44 denotes a reaction vessel, 42 denotes a platinum board that functions as a cathode, 45 denotes a power source for applying an anodization voltage, and 46 denotes an ampere meter for measuring the anodization current. Although not shown in the drawing, a computer for automatically controlling and measuring the voltage and the current is also provided. The sample 41 and the cathode 42 are placed in the electrolyte maintained at a constant temperature by the thermostat. A voltage is applied from the power source to the sample and the cathode so as to perform anodization.

[0048] Examples of the electrolyte used in the anodization include oxalic acid, phosphoric acid, sulfuric acid, chromic acid solutions. Conditions such as anodization voltages and temperatures can be adjusted according to the nanostructure to be formed.

[0049] The anodization process is preferably performed while continuously monitoring the anodization current. For example, in anodizing an aluminum-containing layer formed on

the conductive surface containing at least one element selected from the group consisting of Ti, Zr, Nb, Ta, and Mo, the anodization current changes as indicated by A of Fig. 5. In particular, the anodization current starts to decrease after the aluminum-containing layer is anodized substantially over the entire thickness, and remains substantially constant thereafter. When the anodization is stopped at the time the current is decreased to a substantially constant value, the bottoms of the nanoholes in the anodized film have the structure shown in Fig. 6(a). That is, in most nanoholes, paths comprising elements constituting the conductive surface and connecting the nanohole bottoms to the surface of the conductive material are formed at the bottoms, although the anodized films remain at the bottoms of the nanoholes. When electrodeposition was performed on the nanohole bottoms using the DC power source, electrodeposits were stably formed at nearly every nanohole bottom. This demonstrates that the conditions of the nanoholes were highly uniform.

[0050] On the other hand, when the conductive surface contains Zn or Cu, the anodization current drops after an increase, as shown by B of Fig 5. The state of the nanostructure produced by stopping the anodization at the time of the increase and at the drop after the increase, respectively, was observed with an FE-SEM. The anodized

film locally suffered from crater-shaped damage and had a portion in which the nanoholes disappeared.

[0051] When the conductive surface contains at least one element selected from the group consisting of Au, Pt, Pd, Ni, Fe, Co, and W, the anodization current showed a sharp increase, as shown by C in Fig. 5. After the sharp increase, the anodization was stopped and the nanostructure was observed as described above. Almost all of the nanoholes were lost. When the anodization of the aluminum-containing layer formed on the conductive surface of the substrate, the conductive surface containing at least one element selected from the group consisting of Cu, Zn, Au, Pt, Pd, Ni, Fe, Co, and W, was stopped immediately after the change in anodization current, substantially no damage was observed in the nanoholes, and the conditions of the nanoholes were uniform.

[0052] The reasons for such outcome are not known, and the description below is a presumption. Anodization gradually proceeds from the surface of the aluminum-containing layer toward the conductive surface. When the conductive surface contains at least one element selected from Ti, Zr, Nb, Ta, and Mo, an anodized film remains at each nanohole bottom, and the substances that constitute the conductive surface diffuse into the nanohole bottom via the anodized film, thereby forming a path composed of elements constituting the

conductive surface.

[0053] When this nanostructure is heated or heat-treated in a reducing atmosphere, the conductivity of the nanohole bottoms improves. This is presumably because the substances constituting the paths are reduced. The anodization is preferably stopped after the current has reached a constant value in the anodization current profile shown by A in Fig. 5. This is presumably because the paths are formed at most nanohole bottoms.

[0054] In this embodiment, the anodization is preferably stopped at the time the anodization current reaches 1 mA/cm<sup>2</sup> or less.

[0055] When the conductive surface contains at least one element selected from Au, Pt, Pd, Ni, Fe, Co, and W, the anodization gradually proceeds from the surface of the aluminum-containing layer and reaches the conductive surface. When the electrolyte comes into contact with the conductive surface, electrolysis of the electrolyte at the conductive surface and dissolution of the conductive surface presumably occur, thereby allowing a large current to flow, thus losing nanoholes. When the conductive surface contains Cu or Zn, some degree of electrolysis and dissolution occur when the electrolyte comes into contact with the conductive surface, allowing a relatively large current to flow, thus losing nanoholes. Thus, in this



embodiment, the anodization is stopped immediately after the anodization current showed a change so as to highly effectively prevent loosening of the nanoholes. Alternatively, for example, a current limit may be imposed on the anodization voltage output, or a DC resistance may be provided during the anodization. In imposing the current limit, the limit value is preferably 50 mA/cm<sup>2</sup> or less.

[0056] The following processes d) and/or e) may be performed depending on the use of the nanostructure.

d) Pore widening process

The nanostructure c) after the above-described steps may be immersed in an acid solution, e.g., a phosphoric acid solution, so as to suitably increase the diameter of the nanoholes. The nanohole diameter can be controlled by adjusting the concentration, the process time, and the temperature.

[0057] e) Filling of nanoholes with a metal or a semiconductor

The nanoholes 14 of the structure after c) or d) above may be filled with a metal or a semiconductor. Various techniques using different types of materials may be employed. The nanoholes may be filled with Ni, Fe, Co, Cd, or the like by an electrochemical process (D. Al-Mawlawi et al. J. Mater. Res., 9, 1014 (1994); Masuda et al. HYOMENGIJUTSU, vol. 43, 798 (1992)), or by introduction of

molten metal (C. A. Huber et al. SCIENCE 263, 800 (1994)). Examples of electrochemical methods for filling nanoholes with Fe, Ni, Co include electrolytic deposition using a  $\text{FeSO}_4$  aqueous solution, a  $\text{NiSO}_4$  aqueous solution, or a  $\text{CoSO}_4$  aqueous solution. In Fig. 2e), a filler 15 completely covers the anodized aluminum film 13; alternatively, the nanoholes may be partly filled and put to application.

[0058] As described above, the conductive layer is not necessarily formed when the substrate contains any one of Ti, Zr, Nb, Ta, Mo, Cu, and Zn as the primary component. In such a case, the process a) is omitted from the above-described manufacturing process, and the process b') of forming a layer 12 containing aluminum as the primary component on the substrate 10 may be performed instead to make the sample 41. The processes c) to e) may then be performed.

[0059]

[Examples] The present invention will now be described by way of examples. The present invention is not limited by the examples below, and modifications are possible without departing from the scope of the present invention.

[0060] EXAMPLE 1

Five quartz substrates each having a width of 40 mm and a length of 15 mm were prepared. After the quartz substrates were thoroughly washed with an organic solvent and deionized

water, Ti, Zr, Nb, Ta, and Mo were deposited on the surfaces of the five quartz substrates, respectively, to a thickness of 100 nm by vacuum vapor deposition or sputtering. In depositing the materials other than Ti, Ti was deposited on each substrate to a thickness of 20 nm in advance so as to increase adhesion between glass and the deposit material, thereby giving quartz substrates with conductive surfaces. An aluminum film was then formed on each of the conductive surfaces to a thickness of 1  $\mu\text{m}$  by sputtering.

[0061] Each aluminum film was anodized using the anodization apparatus shown in Fig. 4. Anodization was performed in 0.3 M aqueous oxalic acid (electrolyte) maintained at 17°C by the thermostat at an anodization DC voltage of 40 V while monitoring the anodization current. The results are shown by A in Fig. 5. As shown in Fig. 5, the anodization current started to drop 8 minutes after the start of the anodization. The anodization was stopped 10 minutes after the start since the anodization current dropped to 1 mA/cm<sup>2</sup> or less. In the subsequent pore widening process, the substrates were immersed in a 5 wt.% aqueous phosphoric acid for 30 minutes and washed with deionized water and isopropyl alcohol to obtain nanostructures.

[0062] The surfaces of the nanostructures were observed with a field-emission scanning electron microscope (FE-SEM)

and the cross-sections of the nanostructures were observed with a transmission electron microscope (TEM). According to the observations, nearly all of the nanohole bottoms had paths 16 shown in Fig. 6(a). Moreover, the nanoholes 14 had a diameter of approximately 50 nm and were extremely fine, uniform cylindrical nanoholes. Numerous nanoholes were aligned in parallel rows at a substantially uniform interval of approximately 100 nm. The aluminum films were oxidized over the entire thickness.

[0063] It was also confirmed by elemental analysis that the paths included metals that constituted the conductive surfaces. This is presumably because the anodization gradually proceeded from the surface of the aluminum film and continued even after reaching the conductive surface, thereby allowing the materials constituting the conductive surfaces to disperse into the nanohole bottoms via the anodized layers at the nanohole bottoms. Particularly when the conductive surfaces were composed of Ti or Nb, the anodization current profile showed a steep drop, which suggested formation of more uniform nanoholes.

[0064] COMPARATIVE EXAMPLE 1

Substrates having aluminum films on conductive surfaces were prepared as in EXAMPLE 1 except that the materials of the metal layers constituting the conductive surfaces were changed to W, Fe, Ni, Pd, Pt, and Au. The aluminum films

were then anodized under the same conditions as in EXAMPLE 1. The anodization was continued for 10 minutes, i.e., until the anodization current showed a steep increase, as shown by C in Fig. 5.

[0065] A pore widening process and washing were performed, and the conditions of the nanoholes were observed with a FE-SEM and TEM as in EXAMPLE 1. According to the observations, a moderate to serious degree of damage was found in the nanoholes in the anodized films. The phrase "a moderate degree of damage" means that the nanoholes were partially lost, and the phrase "a serious degree of damage" means that almost all of the nanoholes were lost.

[0066] COMPARATIVE EXAMPLE 2

Substrates having aluminum films on conductive surfaces were prepared as in EXAMPLE 1 except that Cu and Zn were used to form the conductive metal layers. The aluminum films were anodized under the same conditions as in EXAMPLE 1, and the anodization was stopped after 10 minutes, i.e., when the anodization current dropped after an increase, as shown by B in Fig. 5.

[0067] A pore widening process and washing were performed, and the conditions of the nanoholes were observed with a FE-SEM and TEM as in EXAMPLE 1. According to the observations, a small degree of damage was found in the nanoholes in the anodized films. The phrase "a small degree of damage" means

that crater-shaped holes having a diameter of several micrometers were locally observed.

[0068] EXAMPLE 2

Nanostructures were formed as in COMPARATIVE EXAMPLES 1 and 2 except that a current limiter was provided to the anodization power source during the anodization process.

[0069] In particular, the current limiter of the DC power source was operated 5 minutes after the anodization, i.e., when the current profile of the aluminum film showed recovery (indicated by arrow X in Fig. 5). The current limit was set to a value 1.2 times the anodization current value after 5 minutes. Other conditions were the same as in COMPARATIVE EXAMPLES 1 and 2.

[0070] The observation with the FE-SEM demonstrated that the damage to the nanoholes was dramatically reduced compared to the nanostructures of COMPARATIVE EXAMPLES 1 and 2. The observation of the cross-sections demonstrated that, as shown in Fig. 6b), almost all of the nanoholes extended up to the conductive surfaces. Moreover, with Cu, part of the nanohole bottoms was oxidized.

[0071] Each nanostructure was immersed in an electrolyte containing 0.14 M of  $\text{NiSO}_4$  and 0.5 M of  $\text{H}_3\text{BO}_3$ , and Ni was deposited on the nanohole bottoms by electrolyzation using a carbon counter electrode. Nearly all of the nanohole bottoms were filled with Ni using a low voltage ranging from

-1 V to -1.5 V relative to the calomel reference electrode. The electric conductivity between nickel in the nanoholes and the conductive surface was examined. The electrical connection between the conductive surface and nickel filling the nanoholes was satisfactory.

[0072] EXAMPLE 3

This example describes anodization-current monitoring during the manufacture of a nanostructure using a metal substrate.

[0073] In this example, the following was prepared as samples.

Sample 3-1: A conductive layer composed of Mo having a thickness of 1  $\mu\text{m}$  was formed on a Ni substrate having a thickness of 0.5 mm by EB vapor deposition.

Sample 3-2: A Mo board having a thickness of 0.5 mm was used as the substrate, and no conductive layer was formed.

[0074] An aluminum film having a thickness of 1.5  $\mu\text{m}$  was formed by vapor-deposition on the Mo film and the Mo substrate of the samples, respectively. The surface not provided with the aluminum film was coated by epoxy at the portion that would come into contact with the electrolyte. The anodization process was performed as in EXAMPLE 1. During anodization, the profile of the anodization current was constantly monitored. After a current drop indicating the anodization had reached the conductive surface, whether the current had stabilized (arrow Y in Fig 5) was confirmed,

and the voltage application was stopped to end the anodization process.

[0075] The samples of this embodiment were observed with an FE-SEM. The anodized aluminum nanoholes similar to those in Fig. 6(a) were formed on each metal substrate. The depths of the nanoholes of this embodiment were uniform.

[0076] COMPARATIVE EXAMPLE 3

An aluminum board was anodized for 10 minutes under the same conditions as in EXAMPLE 3 so as to obtain a nanostructure having the structure shown in Fig. 3(a). This structure was observed with an FE-SEM as in EXAMPLE 3. According to the observation, there was a variation in depths of the nanoholes.

[0077] EXAMPLE 3 and COMPARATIVE EXAMPLE 3 show that anodized aluminum nanoholes can be formed on a desired substrate by providing a conductive layer composed of the material shown in EXAMPLE 1 as an undercoat. Furthermore, in this example, the thickness of the anodized aluminum nanoholes, i.e., the depth of the nanoholes, was regulated by the thickness of the aluminum film. Accordingly, the depth of the nanoholes was made uniform over large areas.

[0078] According to this example, the anodization current was monitored to determine the end of anodization based on the current profile. Thus, paths were formed with good reproducibility and undesired anodization was avoided.



[0079] EXAMPLE 4

In this EXAMPLE, an n-Si substrate having a diameter of 2 inches was used as the substrate. In Sample 4-1, the conductive layer was a Ti film having a thickness of 200 nm. In Samples 4-1 and 4-2, the conductive layer was a Nb film having a thickness of 200 nm. The thickness of the aluminum film was 500 nm. Another sample was also prepared as COMPARATIVE EXAMPLE 4. The sample of COMPARATIVE EXAMPLE 4 was without any conductive layer and had a partly anodized aluminum film having the structure show in Fig. 3b).

[0080] The processes of c) anodization and d) pore widening were performed as in EXAMPLE 1. Sample 4-3 was heated at 500°C for 1 hour in a reducing atmosphere containing 2% H<sub>2</sub> and 98% He after the anodization.

[0081] e) Filling of nanoholes

The sample subjected to the processes up to the pore widening and a carbon counter electrode were immersed in an electrolyte containing 0.14 M of NiSO<sub>4</sub> and 0.5 M of H<sub>3</sub>BO<sub>3</sub> to deposit Ni on the nanohole bottoms.

[0082] In COMPARATIVE EXAMPLE 4, a voltage of -15 V or more was required for electrodeposition, and the reproducibility of the deposition was poor. In Samples 4-1, 4-2, and 4-3, Ni uniformly filled the nanoholes over the entire surface of each sample at a low voltage ranging from -1 to -1.5 V relative to the calomel electrode. The structure shown in

Fig. 7(a) was observed using the FE-SEM. The cylindrical nanoholes having a diameter of approximately 50 nm were filled with Ni, and numerous Ni-filled nanoholes were aligned in parallel rows at a substantially uniform interval of approximately 100 nm. Particularly, Sample 4-3, which was prepared by depositing Ni to partly fill the nanoholes shown in Fig. 7(b) while controlling the amount of deposition, showed a small variation in amount of fillers among the nanoholes.

[0083] The reason for this is presumably as follows. During the electrodeposition inside the nanoholes, it is essential that the deposition reaction proceed rapidly at the nanohole bottoms. In COMPARATIVE EXAMPLES, however, the barrier layer 32 at the nanohole bottom shown in Fig. 3b) obstructed the reaction, whereas in EXAMPLES, the Ni deposition reaction proceeded smoothly at the hole bottom due to the presence of the path 16 that functions as a conduction path at the nanohole bottom.

[0084] Moreover, in Sample 4-3, since the paths at the nanohole bottoms were reduced by heating in a reducing atmosphere (hydrogen), the conducting property at the nanohole bottoms were presumably improved. The electric conductivity between the Ni filler and the conductive layer was examined, and the results showed that the electrical connection between the conductive layer and the filler was

sufficient in Samples 4-1, 4-2, and 4-3.

[0085] EXAMPLE 5

In this Example, a quartz glass substrate was used as the substrate. In Sample 5-1, a Nb film having a thickness of 1  $\mu\text{m}$  was used as the conductive layer. In Sample 5-2, a Ti film having a thickness of 1  $\mu\text{m}$  was used as the conductive layer. In Sample 5-3, a Cu film having a thickness of 1  $\mu\text{m}$  was used as the conductive layer. In Sample 5-4, a Pt film having a thickness of 1  $\mu\text{m}$  was used as the conductive layer. In Sample 5-5, a Co film having a thickness of 1  $\mu\text{m}$  was used as the conductive layer. The thickness of the aluminum layer was 1  $\mu\text{m}$ . The anodization was performed as in EXAMPLE 1 for Nb and Ti, and as in EXAMPLE 2 for Cu, Pt, Co.

[0086] A sample having the structure shown in Fig. 3(a) prepared by anodizing an aluminum board for 5 minutes was prepared as COMPARATIVE EXAMPLE 5. A sample having the structure shown in Fig. 3(b) prepared by partly anodizing an aluminum film on a quartz glass without any conductive layer was prepared as COMPARATIVE EXAMPLE 6. The thickness of the aluminum film is 1  $\mu\text{m}$ , and the anodization time was continued for 5 minutes.

[0087] Next, the nanoholes with the underlying Nb layer of this Example were heated in a He atmosphere in a temperature ranging from 200°C to 1,100°C for 1 hour, and the structure change was observed with a FE-SEM. The temperature was

increased and decreased at a rate of 5°C/min.

[0088] Considering the melting point of aluminum (630°C), the on-aluminum nanoholes shown in Fig. 3(a) and (b) of COMPARATIVE EXAMPLES 5 and 6 were at a temperature ranging from 200 to 500°C. COMPARATIVE EXAMPLES 5 and 6 had the structure shown in Fig. 3a) and b) before heating, but the anodized films of the samples had film cracks after being heated at a temperature of approximately 300°C or more.

[0089] On the other hand, the structure with the underlying conductive layer of this Example maintained the structure shown in Fig. 1 at high temperatures shown below. The change in structure due to heating was not observed. For example, the nanoholes were uniform, cylindrical nanoholes approximately 50 nm in diameter, and numerous nanoholes were aligned in parallel rows at a substantially uniform interval of approximately 100 nm. The intervals between the holes were uniform.

[0090] Table 1 below shows the temperature range that did not cause damage.

[0091]

[Table 1]

	Material of conductive layer	Upper limit of the temperature that does not cause damage in nanoholes
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Sample 5-1	Nb	1,100°C or more
Sample 5-2	Ti	approximately 600 to 900°C
Sample 5-3	Pt	approximately 500 to 700°C
Sample 5-4	Cu	approximately 400 to 500°C
Sample 5-5	Co	approximately 400 to 500°C

[0092] The above description fully demonstrates that the nanostructure of the present invention including on-conductive-layer nanoholes, particularly those including on-Nb nanoholes, had excellent heat resistance, thereby producing nanoholes that can withstand high temperature processes.

[0093] Moreover, the TEM observation demonstrated that the oxidized aluminum constituting the anodized aluminum nanoholes after heating had superior crystallinity. When the acid resistance of the anodized aluminum nanoholes were compared before and after heating, it was found that the chemical stability was enhanced as a result of the heating.

[0094] EXAMPLE 6

Nanostructures including Nb and Pt conductive surfaces were prepared as in EXAMPLE 5. A metal or a semiconductor was introduced in the nanoholes of the structures by a method similar to that suggested in C. A. Huber et al. In particular, the material to be introduced and each nanostructure were placed in an ample of thin metal, and an

inert atmosphere was charged inside the ample. The temperature was increased to above the melting temperature of the material to be introduced, and the pressure was gradually increased to approximately 4 K bar so as to crush the ample with pressure. Although the temperature of the heating according to Huber et al. was up to 800°C, heating up to a temperature of 1,100°C was possible with the nanostructures of the present invention.

[0095] Accordingly, not only metals such as In, Sn, and Al and semiconductors such as Se, Te, GaSb, Bi<sub>2</sub>, and Te<sub>3</sub> that have a low melting point, but also metals such as Ag, Au, and Cu and semiconductors such as Ge having a high melting point could be introduced. Moreover, in the present invention, because the nanoholes were disposed on the conductive material, the nanoholes could be electrically connected to the conductive layer of Nb or Pt.

[0096]

[Advantages] As described above, the present invention has the following advantages.

- 1) An anodized aluminum film with highly uniform nanoholes can be formed on a desired substrate.
- 2) An anodized aluminum film having highly uniform nanoholes can be formed on a conductive material. In a structure in which nanoholes are filled with a metal or a semiconductor, the metal of the semiconductor can be electrically connected

to the conductive material.

3) An anodized aluminum film with nanoholes having uniform depth over a larger area can be formed.

4) A nanostructure having superior heat resistance can be formed. An anodized aluminum film having superior crystallinity can be formed by heating.

[0097] These advantages allow the anodized aluminum film to be used in various applications, thereby expanding its applicable range. The nanostructure of the present invention can by itself be used as a functional material; however, it may also be used as a base material or a mold for a novel nanostructure.

[Brief Description of the Drawings]

[Fig. 1] Fig. 1 is a schematic view showing the structure of a nanostructure of the present invention and includes (a) a plan view and (b) a cross-sectional view taken along line AA.

[Fig. 2] Fig. 2 is a schematic cross-sectional view of a process for making the nanostructure of the present invention and shows a) the step of forming a conductive layer on a substrate, b) the step of forming a layer containing aluminum as the primary component on the conductive layer, c) the step of forming nanoholes by anodizing the aluminum layer, d) the step of expanding the nanohole diameter by pore widening, and e) the step of

filling the nanoholes with a metal or a semiconductor.

[Fig. 3] Fig. 3 is a schematic view showing the structure of a conventional anodized aluminum film formed on an aluminum board (layer), and includes a) a cross-sectional view when the aluminum board is anodized, b) a cross-sectional view when the aluminum board on the substrate is partly anodized, and c) a perspective view of nanoholes formed on the aluminum board (layer).

[Fig. 4] Fig. 4 is a schematic view for explaining an anodization apparatus.

[Fig. 5] Fig. 5 is a graph indicating different current profiles during anodization.

[Fig. 6] Fig. 6 is a schematic view showing the structure of the nanohole bottoms of nanostructures of EXAMPLES 1 and 3.

[Fig. 7] Fig. 67 is a schematic view showing the structure of the nanohole bottoms of nanohole bottoms of a nanostructure of EXAMPLE 4, and shows (a) the structure in which the nanoholes are completely filled and (b) the structure in which the nanoholes are partly filled.

[Description of the reference numerals]

10: substrate

11: conductive layer

12: layer containing aluminum as the primary component

13: anodized aluminum film



14: nanoholes

15: filler

16: path

17: oxide layer

31: aluminum board

32: barrier layer

40: thermostat

41: sample

42: cathode

43: electrolyte

44: reaction vessel

45: power source

46: ampere meter

[Fig. 1]

(a) 14: nanohole

(b) 14: nanohole

13: anodized aluminum film

10: substrate

11: conductive layer

[Fig. 2]

(a) 10: substrate

11: conductive layer

(b) 10: substrate

11: conductive layer

12: aluminum layer

41: sample

(c) 10: substrate

11: conductive layer

13: anodized aluminum film

14: nanohole

(d) 10: substrate

11: conductive layer

13: anodized aluminum film

14: nanohole

(e) 10: substrate

11: conductive layer

13: anodized aluminum film

14: nanohole

15: filler

[Fig. 3]

13: anodized aluminum film

14: nanohole

32: barrier layer

12 or 31: aluminum board (layer)

(a) 13: anodized aluminum film

14: nanohole

31: aluminum board

32: barrier layer

(b) 13: anodized aluminum film

14: nanohole

31: aluminum board

32: barrier layer

10: substrate

[Fig. 4]

Anodization apparatus

40: thermostat

41: sample

42: cathode

43: electrolyte

44: reaction vessel

45: power source

46: ampere meter

[Fig. 5]

100: anodization current  $I_a$

101: time

102: anodization of aluminum film

103: conductive layer in contact with electrolyte

[Fig. 6]

(a) 10: substrate

11: conductive layer

13: anodized aluminum film

14: nanohole

16: path

17: oxide layer

(b) 10: substrate

11: conductive layer

13: anodized aluminum film

14: nanohole

[Fig. 7]

(a) 10: substrate

11: conductive layer

13: anodized aluminum film

14: nanohole

16: path

17: oxide layer

15: filler

(b) 10: substrate

11: conductive layer

13: anodized aluminum film

14: nanohole

16: path

17: oxide layer

15: filler

[Amendment]

[Date of Filing] November 13, 1998

[Amendment 1]

[Name of Document to be amended] Drawings

[Items to be amended] All of the drawings

[Method of Amendment] Change

[Contents of Amendment]

[Fig. 1]

(a) 14: nanohole

(b) 14: nanohole

13: anodized aluminum film

10: substrate

11: conductive layer

[Fig. 2]

(a) 10: substrate

11: conductive layer

(b) 10: substrate

11: conductive layer

12: aluminum layer

41: sample

(c) 10: substrate

11: conductive layer

13: anodized aluminum film

14: nanohole

(d) 10: substrate

- 11: conductive layer
- 13: anodized aluminum film
- 14: nanohole
- (e) 10: substrate
- 11: conductive layer
- 13: anodized aluminum film
- 14: nanohole
- 15: filler

[Fig. 4]

Anodization apparatus

- 40: thermostat
- 41: sample
- 42: cathode
- 43: electrolyte
- 44: reaction vessel
- 45: power source
- 46: ampere meter

[Fig. 5]

- 100: anodization current  $I_a$
- 101: time
- 102: anodization of aluminum film
- 103: conductive layer in contact with electrolyte

[Fig. 3]

- (a) 13: anodized aluminum film
- 14: nanohole

- 31: aluminum board
- 32: barrier layer
- (b) 13: anodized aluminum film
- 14: nanohole
- 31: aluminum board
- 32: barrier layer
- 10: substrate
- (c) 13: anodized aluminum film
- 14: nanohole
- 32: barrier layer
- 12 or 31: aluminum board (layer)

[Fig. 6]

- (a) 10: substrate
- 11: conductive layer
- 13: anodized aluminum film
- 14: nanohole
- 16: path
- 17: oxide layer
- (b) 10: substrate
- 11: conductive layer
- 13: anodized aluminum film
- 14: nanohole

[Fig. 7]

- (a) 10: substrate
- 11: conductive layer



- 13: anodized aluminum film
  - 14: nanohole
  - 16: path
  - 17: oxide layer
  - 15: filler
- (b)
- 10: substrate
  - 11: conductive layer
  - 13: anodized aluminum film
  - 14: nanohole
  - 16: path
  - 17: oxide layer
  - 15: filler

# 陽極酸化アルミナにもとづく 高規則性メタルナノホールアレー

東京都立大学工学部工業化学科 益田秀樹

## §1 はじめに

電子デバイス、光学デバイスを構築する上で、ナノメートルスケールの規則的な細孔構造を有する材料、ナノチャンネル材料の重要性が増している。これらの材料では従来からの用途、すなわち、分離・濾過、触媒担体などの機能に加え、ナノコンジョイントをはじめとする種々のナノストラクチャーを形成するための出発マトリクスとしての新たな機能に関心が寄せられている。

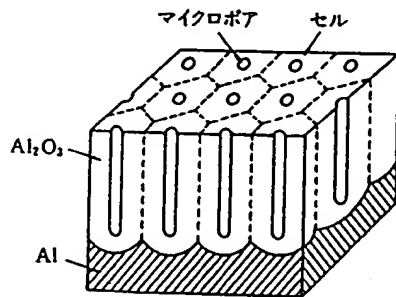
従来、サブミクロン～ナノメートルスケールの規則性を有するチャンネル材料としては、ポーラスガラス、各種ポリマーフィルターメンブレンなどが知られているが、近年、ユニークなポーラス構造を有する材料として陽極酸化ポーラスアルミナに関心が集まっている。陽極酸化ポーラスアルミナは、アルミニウムを酸性電解液中で陽極酸化することにより表面に形成される多孔性酸化皮膜であり、表面処理の分野では「アルマイト」皮膜として古くから知られている。陽極酸化アルミナがもつ幾何学構造は、電子顕微鏡の発達とともに次第に明らかになり、その特異な幾何学構造が表

面処理技術に関連した研究者を中心に関心をもたれてきた。本稿では、これまで他の多孔性材料に比較して関心を持たれることが少なかった陽極酸化ポーラスアルミナと、それをもとに金属をはじめとする種々の材料で作成したナノホールアレー材料について紹介を行う。

## §2 陽極酸化アルミナの形成機構

陽極酸化アルミナの多孔性材料としての最大の特徴は、直行する細孔がほぼ等間隔に平行して形成されるハニカム構造(第1図)をとる点にある<sup>1,2)</sup>。これに加え、細孔径、細孔間隔、細孔深さを比較的自由に制御することができる点も他の材料にない特徴といえよう。無機系の多孔性材料として代表的なポーラスガラスでは、細孔は網目状に屈曲した構造をとっており、各細孔の独立性も確保されていない<sup>3)</sup>。高エネルギー粒子の飛跡を選択的にエッチングすることで細孔を形成するトラックエッチング法メンブレンでは、膜面に垂直に直行した独立細孔の形成が可能であるが、高エネルギー粒子の入射はランダムであり、各細孔の間隔は一定ではない<sup>4)</sup>。また、細孔の重なりを避けるため孔密度を上げることができないという問題点がある。これに対して、陽極酸化アルミナのポーラス構造は、セル構造と呼ばれる皮膜の独特な構造により、直行する独立細孔がほぼ等間隔で配列する理想的なポーラス構造をとる。

陽極酸化アルミナポーラス構造は、アルミニウムを酸性電解液中で陽極酸化する際に酸化皮膜層の形成と、生成した皮膜の溶解が同時に進行する



第1図 陽極酸化ポーラスアルミナのハニカム構造。

ことにより形成される。陽極酸化開始初期、アルミニウムの表面に形成された酸化皮膜の表面には酸による溶解作用で微小なピットがランダムに発生する。陽極酸化の進行とともにこの中のいくつかが優先的に成長し、ほぼ等間隔に配列するようになる。酸化皮膜層の溶解は、皮膜にかかる電場によりイオンの移動が加速されることで促進される。すなわち、いったん、孔が形成された部分では、他の部分に比較して高い電場がかかるため、酸化層の溶解はより促進されることになる。この結果、陽極酸化層には成長とともに選択的に溶解されて孔となる部分と、孔を取り囲むように溶解されずに残される壁の部分形成されることになる。孔をとり囲むシリンダー状の構造は「セル」と呼ばれ、それぞれのセルがほぼ均一な力でバランスしながら成長することにより独特なハニカム構造が形成される。

陽極酸化アルミナが形成される際の幾何学構造は、作成条件により制御することができる。ポラス構造における孔の間隔は陽極酸化時の電圧に、また、孔の深さは陽極酸化時間に比例して増加する。孔径は、浴組成、浴温、電圧などに依存するが、陽極酸化時にこれらの条件を制御することで、あるいは、陽極酸化後のエッチング処理条件を変えることで調節することができる。

### §3 ナノコンポジット材料としての陽極酸化アルミナ

陽極酸化アルミナの特徴ある幾何学構造に着目してこれまでも様々な応用が試みられてきた。これらの応用の中で実用的な見地から最も重要なものは、膜を地金アルミニウムから剝離し、皮膜底部部分をエッチングにより除去して得られる貫通孔膜の精密濾過用フィルターとしての利用である<sup>5,6)</sup>。従来より無機系素材では、均一な孔径の適当なフィルターメンブレンが少ないことから有機系のフィルターが使用できない環境への適用を中心に実用化が進んでいる。

フィルターとしての利用を除けばその応用例は細孔内に種々の物質を取り込ませ、ナノコンポジットとして利用するものが大半を占めている。陽

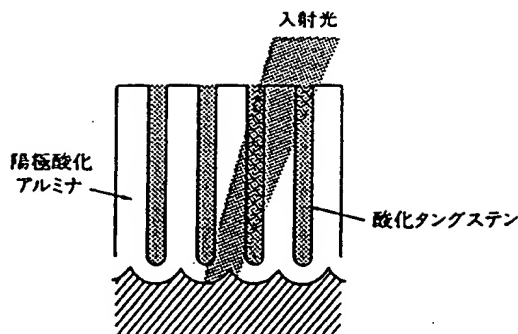


第2図 細孔内へ充填させた金属(Fe)によるシリンダー構造。

極酸化アルミナを用いるコンポジットの代表的なものに細孔内への金属充填による酸化アルミナ/金属コンポジット形成がある。陽極酸化アルミナ細孔内には、電気化学的な手法により種々の金属を析出させることができる。この結果、皮膜内には細孔に対応した金属シリンダーが形成されることになる。第2図には、細孔内に金属を充填した後アルミナ層を選択的に溶解除去して得られたシリンダー構造(Fe)の例を示す。このように形成される酸化アルミナ/金属のコンポジット構造が示す特性として、微細コンポジット構造にもとづく光学特性がある。細孔内に充填された金属は、その種類、充填量、粒径などにより皮膜を様々な着色させる。金属の充填による皮膜の着色は、身近なところでは各種アルミ建材のカラー化や太陽光の選択吸収膜<sup>7)</sup>などに応用されている。

細孔への金属充填の応用としては、その他、シリンダー状に充填された金属を用いた磁気記録媒体が検討されている。陽極酸化アルミナの細孔は膜面に垂直にはほぼ等間隔で形成されることから、細孔内に強磁性金属を充填することにより垂直磁気記録媒体を作成することが可能になる。陽極酸化アルミナを用いた磁気記録媒体に関しては、これまでにいくつかのグループによりその特性が検討されている<sup>8,9)</sup>。

このほか、細孔内への金属、金属酸化物、あるいは有機物の充填が試みられており、EL発光素子<sup>10)</sup>やエレクトロクロミック素子<sup>11)</sup>(第3図)などの表示材料、ポリゲルマン複合体<sup>12)</sup>、光学素子<sup>13)</sup>、



第3図 ポーラス構造への酸化タングステン充填によるエレクトロクロミック素子<sup>11)</sup>。

電極材料<sup>14,15)</sup>などへの応用が報告されている。複合化の手法も電気化学的な金属析出やゾルゲル法など湿式プロセスを中心に多岐にわたっている。

#### §4 陽極酸化アルミナにもとづく メタル、半導体ホールアレー メンブレン

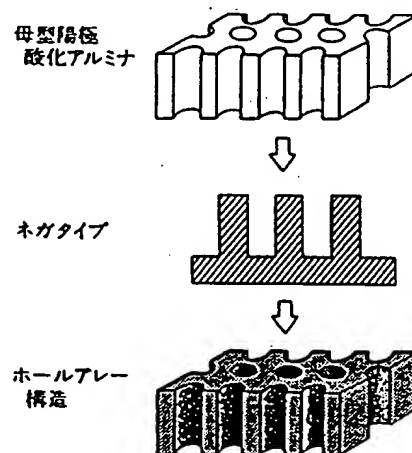
幾何学構造の面では魅力的な特性をもつ陽極酸化アルミナであるが、材質面ではいくつかの問題点を抱えている。陽極酸化アルミナは、化学的な安定性に優れたアルファ型やガンマ型アルミナとは異なり無定形アルミナから構成されている。そのため化学的な安定性、特に、水溶液中での安定性が充分ではなく、長時間水溶液中に浸漬することで水和が進行し細孔の閉塞が起こったり、また、酸性、アルカリ性の溶液中では膜が溶解してしまうといった問題点を抱えていた。このほか機械的にもろく、取り扱いが難しいなどの点が陽極酸化皮膜の応用範囲を広げる上での障害となっていた。

筆者らのグループではこのような陽極酸化アルミナメンブレンの問題点を解決することを目的に陽極酸化アルミナの幾何学構造のみを抽出し、他の物質に置き換える方法について検討を加えてきた<sup>16~24)</sup>。ポーラス構造の完全置き換え手法としては微細な構造、特に、その特徴である高アスペクト比の構造を忠実に転写可能な技術確立することが必要となる。この目的のために筆者らが主として検討を行ってきたのが、陽極酸化アルミナ

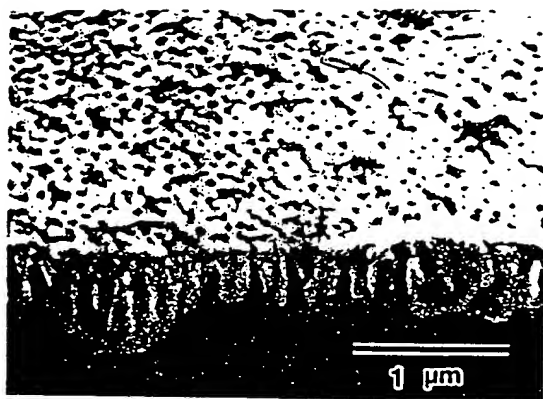
を母型とし、ネガタイプおよびポジタイプを順次作成することで母型と同一の幾何学構造を再現する二段階プロセス(第4図)である。この手法の詳細に関しては、既にいくつかの解説<sup>20,21)</sup>で紹介しているので、ここでは、その概略と特に最近見いだされた高規則性陽極酸化皮膜をもとに作成されたホールアレー構造を中心に述べる。

このプロセスでは、まず、適当な材料を陽極酸化アルミナの細孔内に充填し、陽極酸化アルミナを選択溶解することにより陽極酸化アルミナのネガタイプを作成する。次いでネガタイプに金属、半導体、あるいはポリマーなど目的とする物質を充填し、その後ネガタイプを溶解除去することにより母型と同一の幾何学構造をもつポーラスメンブレンを得る。このプロセスで重要なことは、目的とする物質でポーラス構造を忠実に再現するための素材とプロセスを選択することである。たとえば、プロセスに組み込まれるネガタイプの材料は、母型の幾何学構造を忠実に転写可能であり、同時に最終目的とするポジタイプ材料の充填が容易なものである必要がある。更に、最終目的物に合わせて選択溶解が可能なものである必要がある。

第5図には電析プロセスを用いて作成したCdSホールアレー構造の作成例を示す<sup>22)</sup>。金属のほか、半導体の場合でもネガタイプに充填可能なものであればホールアレー構造の作成が可能である。第5図の例では、ホールアレー構造を形成す



第4図 2段階転写プロセスによるホールアレー構造の作成。



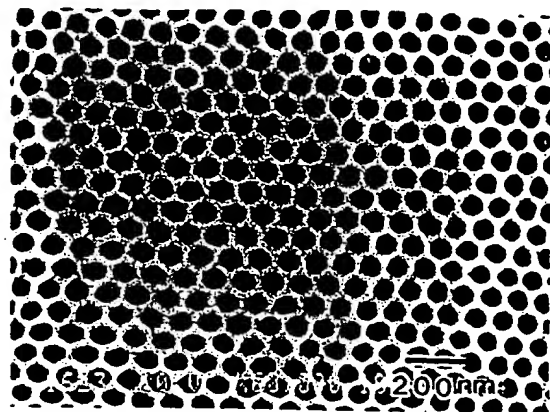
第5図 電解法により作成したCdS ホールアレー。

るCdSは、粒径約150Åの超微粒子から形成されており、太陽電池やセンサーなどへの応用が期待されている。このほか、ゾルゲル法を用いてネガタイプに金属酸化物を充填することによってもTiO<sub>2</sub>、ZnOなどのホールアレー構造の作成が可能である<sup>18)</sup>。

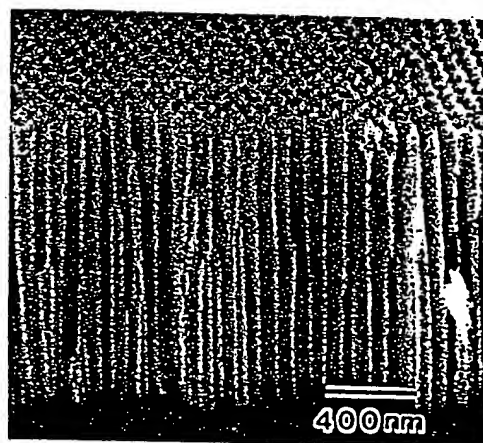
## §5 細孔配列の高規則化

従来知られている陽極酸化アルミナのポーラス構造は、セル構造に由来する高い規則性を有しているものの、実際に得られる皮膜構造は理想的なハニカム構造からはかけはなれたものであった。筆者らは最近、適切な条件で陽極酸化を行うことによりこれまで知られている細孔配列に比べ著しく高規則化し、一定の領域ではほぼ理想的な細孔配列を有する陽極酸化アルミナが得られることを見いだした。陽極酸化アルミナの規則性の向上は、種々の物質でナノホールアレーを作成する上でも目的物質によるホールアレー構造の高規則化につながる。シュウ酸を電解液に用いる場合を例にとれば、40V付近の定電圧条件のもと陽極化成を行うことにより規則化が進行する。セル配列の規則化は陽極酸化時間とともに進行し、長時間陽極酸化を行うことによりセルがほぼ理想的な配置をとるようになる。現在のところセル配列の高規則化の機構の詳細は明らかではないが、得られる陽極酸化アルミナのセル配列は自然に形成される構造としては例外的に高い規則性をもっているといえる。

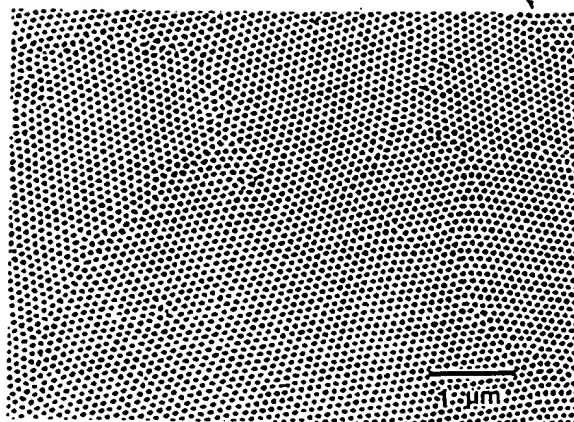
第6図、第7図、第8図には、このような条件で得られた陽極酸化皮膜をもとに作成したPtのホールアレー構造を示す。このホールアレーの場



第6図 高規則構造を有するPtホールアレー。



第7図 Ptホールアレー(破断面SEM写真)。

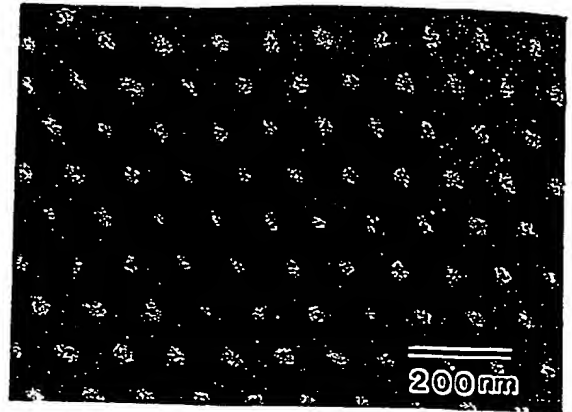


第8図 Ptホールアレー(低倍SEM写真)。

合、ネガティブタイプに高分子材料、ポジティブにはPtの無電解析出反応を用いている。孔径70 nmの直行細孔が100 nmの周期で規則的に配列している様子がわかる。第8図に示す低倍率のSEM写真は、規則化した領域の中でも広いものの一つを示したものであるが、理想的な規則配列部分は、数 $\mu\text{m}$ 四方のドメインを形成しており、これらのドメインが隣接する部分に欠陥が集中している。これは、陽極酸化の進行にともない理想的なセル配列した部分が周辺の不規則部分を取り込みながら成長し、一定の大きさのドメインを形成して隣接することによるものと考えられる。

このように高規則化した陽極酸化アルミナを用いることでホールアレー構造以外にも種々の規則構造の形成が可能になる。第9図には、このような構造の一例として陽極酸化アルミナを真空蒸着用のマスクとして用いたドットアレー構造の作成例を示す<sup>25,26)</sup>。ナノメートルサイズの金属、あるいは半導体を基板上に配列したナノドットアレーの作成は、発光素子など開発のための要素技術として様々な方法が提案されている。アレーの作成にあたっては、ドットの大きさ、形状、間隔を一定にすることが重要となるが、陽極酸化アルミナを蒸着マスクとして用いることで、規則的な孔配列に対応したドットアレー構造が簡便に得られることが期待される。第9図は、陽極酸化アルミナをマスクとして用いSi基板上に形成したAuのドットアレーのSEM写真であるが、直径約40 nmのドットが約100 nmの間隔でほぼ規則的に配列している様子が観察できる。マスクとして用いる陽極酸化アルミナの細孔配列は、一定の欠陥をもつことから広い範囲では理想配列とはならないが、ほぼ等間隔でドットを形成することが可能であり、マスクに用いる陽極酸化アルミナの孔径を変化させることにより、より微小(約30 nm)なドットの作成が可能なが確認されている。

この方法では蒸着可能なものであれば、比較的大きな面積でドットアレーの形成が可能であり、リソグラフィーの場合のようにプロセスに伴う基板ダメージもないことから様々な系への応用が考えられる。



第9図 Si基板上に形成されたAuナノドットアレー構造。

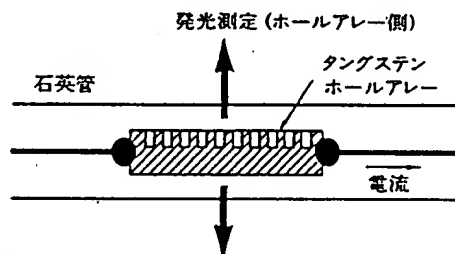
## §6 ホールアレー構造の応用

二段階プロセスにより種々の物質で作成されたホールアレー構造は、従来の材料にない特徴を有し様々な応用が期待される。以下にホールアレー構造の応用例のいくつかについて紹介する。

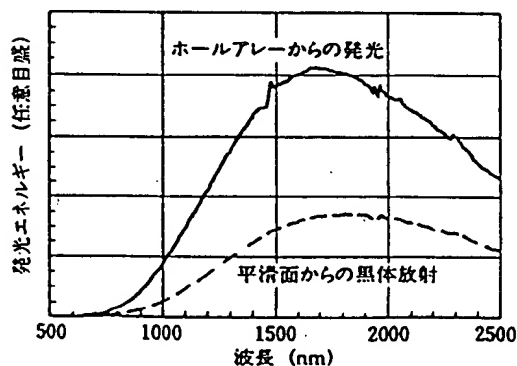
陽極酸化アルミナをもとに作成したメタルホールアレーの特徴は、既に述べたように孔径の揃った高アスペクト比の細孔構造が得られる点にある。杉本らは、この方法により作成したタングステンホールアレーを用いた波長選択的な発光素子についての検討結果を報告している<sup>27)</sup>。平滑な面からの発光スペクトルは、発光体の温度により決定される黒体放射スペクトルとなる。これに対し、表面に一定の大きさのホールアレーを形成した場合には、発光スペクトルは黒体放射スペクトルからはずれ、孔径に依存したものとなることが予測されていた。この予測に従えば、孔径を制御したホールアレー構造を作成することにより波長選択性を有する発光体が形成できることになる。杉本らは陽極酸化アルミナを母型に上述の二段階転写プロセスを用い、孔径約200~400 nm、深さ2~4 $\mu\text{m}$ の細孔アレーを有するタングステンホールアレーを作成し、1400 Kにおける発光スペクトルの測定を行った(第10図)。この結果、ホールアレーからの発光は、平滑面からの黒体放射スペクトルに比較して可視光域の比率が増加したスペクトルを示すことが確認されている(第11図)。タ

ングステンは電析プロセスでは形成困難なことから、ホールアレー構造の作成には低圧 CVD プロセスによるタングステン充填が用いられている。

このほか金属ホールアレーは、微細な構造にもとづく特有な光学特性を示す。既に述べたように陽極酸化アルミナの細孔内に金属を充填した場合、金属微粒子が誘電体(酸化アルミニウム)内に分散した構造となり、金属の種類、粒径などに依存した分光特性を示すことが知られており、多くの解析例が知られている<sup>7,28)</sup>。二段階転写プロセスで形成されたホールアレーは、酸化アルミニウム/金属微粒子系とは異なった構造をとるが、やはりバルク金属とは違った光学特性が観察される。たとえば、Au ホールアレーの場合、通常の Au に比較し赤色化が観察され、この変化は平滑な Au に比較したとき反射スペクトルの長波長側へのシフトとして測定される。ホールアレー構造の光学特性の詳細に関しては、現在検討を進めている段階であるが、制御された幾何学構造表面が作成できることから、光学特性の解析のモデル系としての応用が期待できる。



第10図  
タングステンホールアレーを用いた発光体<sup>27)</sup>。



第11図 タングステンホールアレー構造からの発光スペクトル<sup>27)</sup>。

母型とする陽極酸化アルミナの細孔径は、200 nm~5 nm の範囲で制御することができる(ただし高規則化した構造が得られる範囲はこれよりも狭い)。したがって、この範囲では金属、あるいは、半導体のホールアレー構造の作成が原理的には可能である。これらの細孔径の範囲は通常の分子に比較した場合かなり大きい、分子の中でも大きな分子量を有する酵素などと比較した場合にはほぼ同程度となる。したがって、これらの分子に対しては、分子サイズに合わせたホールアレー構造の設計が可能となる。このような一種の人工モレキュラーシーブ系構築の例として、Pt で作成したホールアレー電極へのグルコースオキシダーゼ取り込み特性について検討を行った<sup>29)</sup>。グルコースオキシダーゼは、ブドウなどの酸化を触媒する酸化還元酵素の一種であるが、Pt 電極の細孔径を変化させることにより、触媒反応にもとづく応答電流値の変化が観察され、酵素分子の細孔への取り込みが制御されていることを示唆する結果が得られている。

## §7 おわりに

自己規則化構造の代表ともいえる陽極酸化アルミナにもとづいた種々のホールアレー構造の作成について紹介をした。陽極酸化アルミナ、あるいはそれをもとにした種々ホールアレー構造は、これまで物理、あるいは、エレクトロニクスなどの分野ではあまり馴染みがなかったものであるが、本稿で紹介したように他の材料にはない特徴を有しており、今後様々な分野での利用が期待される。

金属をはじめとする種々の材料でホールアレー構造を作成する多段階プロセスは、ナノメートルスケールの微細な幾何学構造を転写プロセスにより再現することで、新規な材料を得ようとするアプローチの一つのモデル系と考えることができる。本稿がこのような新しい材料開発手法発展の一助となれば幸いである。

## 〔参考文献〕

- 1) F. Keller, M. S. Hunter, and D. L. Robinson: J. Electrochem. Soc., 100 (1953) 411.

- 2) J. P. O'Sullivan and G. C. Wood: Proc. Roy. Soc. Lond., A, 317 (1970) 511.
- 3) 江口清久: 表面 25 (1987) 184.
- 4) T. D. Brock: *Membrane Filtration* (Science Tech, New York, 1983).
- 5) K. Itaya, S. Sugawara, K. Arai, and S. Saito: J. Chem. Eng. Jpn., 17 (1984) 514.
- 6) R. Furneaux, W. R. Rigby, and A. P. Davidson: Nature, 337 (1989) 147.
- 7) C. G. Granqvist, A. Anderson, and O. Hunderi: Appl. Phys. Lett., 35 (1979) 268.
- 8) S. Kawai, and R. Ueda: J. Electrochem. Soc., 122 (1975) 32.
- 9) 津屋 昇, 徳島忠夫, 白木 真, 涌井幸夫, 斎藤兆古, 中村秀男: 固体物理 21 (1986) 816.
- 10) I. Mizuki, H. Masuda, and N. Baba: Advanced Mat. 15A (1994) 381.
- 11) N. Baba, T. Yoshino, and K. Kono: *Advanced Metal Finishing Technology in Japan*, ed. by N. Baba (Technocrat, Tokyo, 1980) p. 129.
- 12) 地渡美奈子, 吉野隆子, 益田秀樹, 岡野光俊, 浜野裕司: 表面技術協会第93回大会講演要旨集, p. 268 (1996).
- 13) M. Saito, M. Kihara, T. Taniguchi, and M. Miyagi: Appl. Phys. Lett., 55 (1989) 607.
- 14) C. J. Müller and M. Majda: J. Am. Chem. Soc., 107 (1985) 3118.
- 15) K. Uosaki, K. Okazaki, H. Kita, and H. Takahashi: Anal. Chem., 62 (1990) 652.
- 16) H. Masuda, T. Tanaka, and N. Baba: Chem. Lett., 1990 (1990) 621.
- 17) H. Masuda, K. Nishio, and N. Baba: Thin Solid Films, 223 (1993) 1.
- 18) H. Masuda, K. Nishio, and N. Baba: Jpn. J. Appl. Phys., 31 (1992) L1775.
- 19) 益田秀樹, 西尾和之, 馬場宜良: 表面技術 43 (1992) 798.
- 20) 益田秀樹: 表面技術 46 (1995) 420.
- 21) 益田秀樹: フルトビア 25, No. 7 (1995) 41.
- 22) P. Hoyer, N. Baba, and H. Masuda: Appl. Phys. Lett., 66 (1995) 2700.
- 23) 益田秀樹, 中山靖之, 福田健二, 馬場宜良: 表面技術協会第89回大会講演予稿集, p. 107 (1994).
- 24) H. Masuda and K. Fukuda: Science, 268 (1995) 1466.
- 25) 佐藤昌宏, Patrik Hoyer, 益田秀樹: 電気化学協会第62回大会講演要旨集, p. 156 (1995); '95秋季大学講演要旨集 p. 69 (1995).
- 26) H. Masuda and M. Satoh: Jpn. J. Appl. Phys., 35 (1996) L126.
- 27) M. Sugimoto, H. Fukushima, T. Fujioka, T. Marushima, and M. Toho: J. Lighting and Vis. Environ. 18, No. 2 (1994).
- 28) D. G. W. Goad and M. Moskovits: J. Appl. Phys., 49 (1978) 2929.
- 29) H. Masuda, T. Mizuno, N. Baba, and T. Ohomori: J. Electroanal. Chem., 368 (1994) 333.

## お・知・ら・せ 新技術事業団創造科学技術推進事業(ERATO) 1996年 大阪研究報告会

日時 5月30日(木) 13:00~16:35 入場無料  
大阪科学技術センター8階大ホール  
大阪市西区靱本町1丁目  
(地下鉄四ツ橋線本町駅下車北へ徒歩3分,  
うつば公園北角)

### 内容

新技術事業団創造科学技術推進事業の大阪研究報告会が今年も開催されます。この事業は、優れたプロジェクトリーダーの下に国内外から若手研究者が参集して、新しい科学技術を切り拓く基礎研究を進めるもので、発足以来15年目を迎えます。これまでに25プロジェクト(以下PJと略号)が5年間の研究期間を終了して、研究成果の展開期にあり、現在は20PJが研究を実施中です。

この報告会では、研究を実施中の次のPJについて、研究成果などを講演とパネルで解り易く説明します。

- ・柳田生体運動子PJ(柳田敏雄大阪大学教授ほか)
- ・田中固体融合PJ  
(田中俊一郎東芝研究開発センター研究主幹ほか)
- ・岡山細胞変換PJ(岡山博人東京大学教授ほか)
- ・舩本単一量子点PJ/加藤たん白生細胞PJ/土居  
バイオアシンメトリPJ/御子柴細胞制御PJ  
(パネル展示説明)

問い合わせ先

〒332 川口市本町4-1-8  
新技術事業団 創造科学技術推進事業部  
TEL 048-226-5630, FAX 048-226-5653